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$$G(\mathbf{r}) = Y_{\lambda\mu}(\hat{r})f(r)$$

in which $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function. The

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The Use of Fourier Transform Methods for the Evaluation of Coefficients in a Taylor Series to Arbitrary Order

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Summary

We present a new formulation of the Taylor series for a class of functions which can be expressed as the product of a purely angular and purely radial part, viz.,

$$G(\underset{\sim}{r}) = Y_{\lambda\mu}(\hat{r})f(r)$$

in which $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function. The formulation is based upon the use of the Fourier transform of the function to be expanded. The general expression for the Taylor series which we obtain is similar in form to the Laplace expansion for the Coulomb potential. Thus, Taylor series can be developed for arbitrary functions along lines which are similar to the multipolar expansions in the electromagnetic theory. Such expansions are easily adapted to the symmetry of a collection of sources.

1. Introduction

Our purpose in this paper is to present a new and powerful method of handling the expansion of a class of functions in a Taylor series. The elements of this class are simply those functions which can be expressed as a product of a purely radial and purely angular part: viz.,

$$G(r) = Y_{\lambda\mu}(\hat{r})F(r) \tag{1.1}$$

in which $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function. We proceed to derive the general term of the Taylor series to any arbitrary order. We are able to show that given the Fourier transform of any well-behaved function (or generalized function), it is possible to obtain the specific form of an arbitrary term in the series.

These results extend and generalize an initial effort which was presented elsewhere by us (Schmidt, Pons, and McKinley, 1980). In particular, by more laborious means, we derived specific formulae for the first and second order terms of the Taylor series. The method which we used in that earlier work we found not to generalize easily to the expression of a general term for the Taylor series. The results of this paper contain exactly the results reported previously (Schmidt, et al., 1980).

We find several reasons for undertaking the development of this new expression of the Taylor series. Foremost is our need to consider the displacement of a particle about a point of equilibrium which simultaneously is also a centre of symmetry for a collection of sources (Schmidt, et al., 1980). Thus, we need to consider

a form of the Taylor series expansion of an arbitrary function which exploits the symmetries of the system in the same manner as is customarily done for the electrostatic potential through the use of the Laplace expansion (cf., Jackson, 1962). These symmetries are most effectively handled through the use of expansions which depend upon the spherical harmonic functions. Hence, it is natural to consider the use of Fourier transforms.

Often, and for molecular physics in particular, it is necessary to consider approximations of complicated functions. This is especially true of potential energy functions which are derived from molecular integrals. The analysis of the mechanics of molecular vibrations, for example, commonly depends upon approximations which replace the exact potential energy functions with harmonic replicas. It is universally known, of course, that these harmonic approximations are adequate only when applied to the analyses of the molecular low-lying vibrational states.

It is frequently of interest to examine higher order terms in order to assess the accuracy of the harmonic approximation. In some cases, higher order terms are required in order to establish limits of stability for mechanical systems. For a relatively simple, complete function, it is possible to extract cartesian harmonic and higher order terms as individual terms in a Taylor series. Realistic potential energy functions, however, often contain fairly complicated angular dependencies. These angular dependencies reflect the complicated character of the environment which surrounds a particular particle (atom or molecule) of interest [see, for example, Briels (1980)]. For these functions, the forming of the Taylor series ceases to be a simple matter.

The usual representation of the Taylor series presents the determination of the coefficients as a sequence of differentiations. These operations are applied to the function the expansion of which is required. It is possible in principle to make repeated use of Rose's (1957) formula for the gradient to determine these coefficients in terms of the basis vectors of the spherical tensors. In reality, however, any actual attempt to apply that formula, even to the simplest of functions, quickly becomes unmanageable. It is tedious even to determine the harmonic terms for the series.

In contrast, we are able to obtain the coefficients of the Taylor series after the evaluation of only a single form of radial integral. The strength of the method, therefore, is a transparent compactness and flexibility in terms of ease of application. This strength is illustrated by several examples in a separate paper (McKinley and Schmidt, 198_ b).

The outline of this paper is the following. In section 2 we consider the single centre expansion of a function into a Taylor series. A particular form of our result replaces differentiations with integrations. For complicated functions, which possess well-defined Fourier transforms, these integrals prove easier to consider and evaluate than is the case of the consideration of the multivariate differentiation of the function directly.

In section 3, based on the use of the results of section 2, we present a derivation of Rose's (1957) formula for the gradient operation. A consistency between Rose's work and ours is established. In addition, we use the differential raising and lowering operators for the spherical Bessel functions to re-establish a differential form for the Taylor series coefficients. This differential form

is consistent with the angular dependencies of the integral form and with the symmetries of the spherical harmonic functions. It is clear from the differential form obtained that in many instances the integral representation is indeed the simpler way to approach the determination of coefficients in a Taylor series.

In section 4 we consider the Taylor series as an expansion about two centres. It is possible to consider the general development of any well-behaved function as an expansion about two or more centres. The Carlson-Rushbrooke (1950) expansion of the free-space Green function is such an example. In section 4 we establish a parallel treatment of the Taylor series. We limit our considerations, however, only to two centres. In this section we also show that as the two centres coalesce, the resulting form is consistent with the single centre form of the Taylor series.

Finally, in the last section we mention the limiting forms for scalar functions. Whereas for the general case, for a general angular dependence, the integral form of the Taylor series seems to be the simpler route to follow, for a scalar function, we find the resulting differential form is equally simple, if not simpler, to use. Our form of the Taylor series in its differential representation for a scalar function, however, does not bear a close resemblance to the cartesian differential form. Our form preserves the angular dependencies as arguments of the Legendre polynomials. Differentiation is applied only to the radial part of the function.

2. The Taylor Series for the Expansion about one Centre

We develop the Taylor series for functions which are separable into purely radial and purely angular parts, viz.,

$$G(\underset{\sim}{r}) = F(r)Y_{\lambda\mu}(\hat{r}) \tag{2.1}$$

where $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function. Still more general functions could be expressed as superpositions of such functions. The function $G(\underset{\sim}{r})$ admits a Fourier transform:

$$G(\underset{\sim}{r}) = (2\pi)^{-3}\int d^3k\ f(k)Y_{\lambda\mu}(k)\exp(-i\underset{\sim}{k}\cdot\hat{r}) \tag{2.2}$$

where f(k) is given by

$$f(k) = 4\pi i^{\lambda}\int_0^{\infty} dr\ r^2 F(r) j_{\lambda}(kr) \tag{2.3}$$

and $j_{\lambda}(x)$ is the spherical Bessel function of the first kind.

The function at the displaced point $\underset{\sim}{r} + \underset{\sim}{c}$ is given by the vectorial Taylor series (Band, 1959)

$$G(r+c) = \sum_{n=0}^{\infty} \frac{1}{n!} (\underset{\sim}{c}\cdot\nabla)^n G(\underset{\sim}{r}). \tag{2.4}$$

Consider now the general term in this series with $G(r)$ given by its F.t.:

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = \frac{1}{(2\pi)^3 n!}\int d^3k\ f(k)Y_{\lambda\mu}(\hat{k})(-i\underset{\sim}{c}\cdot\underset{\sim}{k})^n \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r})$$

$$= \frac{(-ic)^n}{(2\pi)^3 n!}\int d^3k\ k^n f(k)Y_{\lambda\mu}(\hat{k})(\hat{c}\cdot\hat{k})^n \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}). \quad (2.5)$$

Here, $\hat{c}\cdot\hat{k}$ is the cosine of the angle between the unit vectors $\hat{c}$ and $\hat{k}$. The n*th* power of this quantity can be expanded in Legendre polynomials of the same argument (Morse and Feshback, 1953)

$$(\hat{c}\cdot\hat{k})^n = \sum_{\ell} A_{n\ell} P_{\ell}(\hat{c}\cdot\hat{k}). \quad (2.6)$$

The coefficients $A_{n\ell}$ are given by

$$A_{n\ell} = \frac{2\ell+1}{2}\int_{-1}^{+1} dx\ x^n P_{\ell}(x)$$

$$= 0,\ \ell>n \text{ or } n-\ell \text{ odd}$$

$$= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!},\quad \ell\leq n \text{ and } n-\ell \text{ even}. \quad (2.7)$$

We now introduce the Rayleigh expansion,

$$\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) = \sum_{L}(-i)^L(2L+1)j_L(kr)P_L(\hat{k}\cdot\hat{r}), \quad (2.8)$$

and the addition theorem for the spherical harmonic functions,

$$P_L(\hat{k}\cdot\hat{r}) = \frac{4\pi}{2L+1}\sum_{M} Y^*_{LM}(\hat{k})Y_{LM}(\hat{r}), \quad (2.9)$$

so that we have

$$\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) = 4\pi \sum_{L,M} (-i)^L j_L(kr) Y^*_{LM}(\hat{k}) Y_{LM}(\hat{r}) \tag{2.10}$$

and

$$(\hat{c}\cdot\hat{k})^n = 4\pi \sum_{\ell,m} (2\ell+1)^{-1} \Lambda_{n\ell} Y^*_{\ell m}(\hat{k}) Y_{\ell m}(\hat{c}). \tag{2.11}$$

With these substitutions, Equation (2.5) becomes

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = \frac{2c^n}{n!} \sum_{L,M,\ell,m} (-i)^{L+n} (2\ell+1)^{-1} \Lambda_{n\ell} Y_{LM}(\hat{r}) Y_{\ell m}(\hat{c})$$

$$\times \int_0^\infty dk\ k^2 \int_{4\pi} d\Omega_k k^n f(k) j_L(kr) Y_{\lambda\mu}(\hat{k}) Y^*_{LM}(\hat{k}) Y^*_{\ell m}(\hat{k}). \tag{2.12}$$

The angular integral is the well-known integral over three spherical harmonic functions (Rose, 1957)

$$\int_{4\pi} d\Omega_k Y_{\lambda\mu}(\hat{k}) Y^*_{LM}(\hat{k}) Y^*_{\ell m}(\hat{k}) = \left[\frac{(2\ell+1)(2L+1)}{4\pi(2\lambda+1)}\right]^{1/2} (L\ell 00|\lambda 0)(L\ell Mm|\lambda\mu) \tag{2.13}$$

where $(L\ell Mm|\lambda\mu)$ is the Clebsch-Gordan coefficient. We also introduce a quantity defined by the remaining radial integral:

$$I_{nL}(r) = \frac{1}{(2\pi)^3}\int_0^\infty dk\ k^{n+2} f(k) j_L(kr). \tag{2.14}$$

Altogether, we have found the following expression for the general term in the Taylor series:

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = (4\pi)^{3/2}\ \frac{c^n}{n!} \sum_{L,M,\ell,m} (-i)^{L+n} \Lambda_{n\ell} Y_{LM}(\hat{r}) Y_{\ell m}(\hat{c})$$

$$\times\left[\frac{2L+1}{(2\ell+1)(2\lambda+1)}\right]^{1/2}(L\ell 00|\lambda 0)(L\ell Mm|\lambda\mu)I_{nL}(r). \qquad (2.15)$$

The most frequently used cases will be those of the lowest order. For n=1, ℓ can only be 1 and $A_{11}=1$. We have then

$$\underset{\sim}{c}\cdot\underset{\sim}{\nabla}G(\underset{\sim}{r}) = (4\pi)^{3/2}c\sum_{L,M,m}(-i)^{L+1}Y_{LM}(\hat{r})Y_{1m}(\hat{c})\left[\frac{2L+1}{3(2\lambda+1)}\right]^{1/2}$$

$$\times(L100|\lambda 0)(L1Mm|\lambda\mu)I_{1L}(r). \qquad (2.16)$$

A special application of this is to find an equilibrium condition, which can be expressed as $\underset{\sim}{c}\cdot\underset{\sim}{\nabla}G(\underset{\sim}{r}) = 0$, for any $\underset{\sim}{c}$, or as

$$0 = \sum_{L,M}(-i)^{L}Y_{LM}(\hat{r})(2L+1)^{1/2}(L100|\lambda 0)(L1Mm|\lambda\mu)I_{1L}(r). \qquad (2.17)$$

For n=2, ℓ can be either 0 or 2 with $A_{20}=1/3$ and $A_{22}=2/3$. We have then

$$\frac{1}{2}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^2G(\underset{\sim}{r}) = \frac{(4\pi)^{3/2}}{2}c^2\left[\frac{1}{3}(-i)^{\lambda+2}Y_{\lambda\mu}(\hat{r})Y_{00}(\hat{c})I_{2\lambda}(r)\right.$$

$$+\frac{2}{3}\sum_{L,M,m}(-i)^{L+2}Y_{LM}(\hat{r})Y_{2m}(\hat{c})\left[\frac{2L+1}{5(2\lambda+1)}\right]^{1/2}(L200|\lambda 0)(L2Mm|\lambda\mu)$$

$$\left.\times I_{2L}(r)\right]. \qquad (2.18)$$

These lowest order terms are obviously easy to evaluate, but even the general term [Equation (2.15)] is not intrinsically more difficult. This simplicity traces back to Equation (2.11) which is

an especially simple example of the expansion of an invariant into irreducible forms (Fano and Racah, 1959).

3. The Formula for the Gradient

In this section we verify that the first order term, eqn (2.16), is equivalent to the usual gradient formula (Rose, 1957).

We begin by evaluating the Clebsch-Gordan coefficient $(L100|\lambda 0)$ in expression (2.16). This coefficient restricts the parity of L as well as limits its range. We have

$$\begin{aligned}(\lambda-1,100|\lambda 0) &= \left(\frac{\lambda}{2\lambda-1}\right)^{1/2}\\ (\lambda+1,100|\lambda 0) &= -\left(\frac{\lambda+1}{2\lambda+3}\right)^{1/2};\end{aligned} \tag{3.1}$$

all other values of L yield zero. We now write

$$\begin{aligned}\underset{\sim}{c}\cdot\underset{\sim}{\nabla}G(\underset{\sim}{r}) = (-i)^{\lambda}\frac{(4\pi)^{3/2}}{\sqrt{3}}\sum_{M,m}\Bigg\{&\left(\frac{\lambda}{2\lambda+1}\right)^{1/2}(\lambda-1,1Mm|\lambda\mu)Y_{\lambda-1M}(\hat{r})Y_{1m}(\hat{c})\\ &\times I_{1,\lambda-1}(r) + \left(\frac{\lambda+1}{2\lambda+3}\right)^{1/2}(\lambda+1,1Mm|\lambda\mu)Y_{\lambda+1M}(\hat{r})Y_{1m}(\hat{c})I_{1,\lambda+1}(r)\Bigg\}\end{aligned} \tag{3.2}$$

We handle the angular and radial factors separately. The standard definitions of the vector spherical harmonic functions are (rose, 1957)

$$\underset{\sim}{T}_{\lambda,\lambda\pm1,\mu}(\hat{r}) = \sum_{M,m}(\lambda\pm1,1Mm|\lambda\mu)Y_{\lambda\pm1M}(\hat{r})\underset{\sim}{\xi}_m \tag{3.3}$$

where the quantities $\underset{\sim}{\xi}_m$ are the basis vectors for the spherical

tensors (Rose, 1957). The scalar product of (3.3) with the vector $\underset{\sim}{c}$ is

$$\underset{\sim}{c}\cdot\underset{\sim}{T}_{\lambda\lambda\pm 1\mu}(\hat{r}) = \sum_{M,m}(\lambda\pm 1 1Mm|\lambda\mu)Y_{\lambda\pm 1m}(\hat{r})\underset{\sim}{c}\cdot\underset{\sim}{\xi}_{m} \tag{3.4}$$

$$= \sqrt{4\pi/3}\sum_{M,m}(\lambda\pm 1 1Mm|\lambda\mu)Y_{\lambda\pm 1M}(\hat{r})Y_{1m}(\hat{c}).$$

On the other hand, for the radial part we consider the following. In the definition of $I_{1\lambda\pm 1}(r)$ we use the standard operators for lowering and raising the index of the spherical Bessel functions (Morse and Feshback, 1953, and Infeld and Hull, 1951). Thus,

$$(2\pi)^3 I_{1\lambda-1}(r) = \int_0^\infty dk\ k^3 f(k) j_{\lambda-1}(kr)$$

$$= \int_0^\infty dk\ k^3 f(k)\left[\frac{\lambda+1}{kr}j_\lambda(kr) + \frac{d}{d(kr)}\ j_\lambda(kr)\right]$$

$$= \left[\frac{\lambda+1}{r} + \frac{d}{dr}\right]\int_0^\infty dk\ k^2 f(k) j_\lambda(kr). \tag{3.5}$$

Similarly,

$$(2\pi)^3 I_{1\lambda+1}(r) = \int_0^\infty dk\ k^3 f(k) j_{\lambda+1}(kr)$$

$$= \left[\frac{\lambda}{r} - \frac{d}{dr}\right]\int_0^\infty dk\ k^2 f(k) j_\lambda(kr). \tag{3.6}$$

At this point, we identify the inverse of eqn (2.5):

$$F(r) = \frac{(-i)^\lambda}{2\pi^2}\int_0^\infty dk\ k^2 f(k) j_\lambda(kr) \tag{3.7}$$

Upon substitution of all of these expressions into eqn (3.2), we find exactly the standard formula for the gradient operation (Rose, 1957):

$$\underset{\sim}{c}\cdot\underset{\sim}{\nabla}G(\underset{\sim}{r}) = \underset{\sim}{c}\cdot\underset{\sim}{\nabla}[Y_{\lambda\mu}(\hat{r})F(r)]$$

$$= \left(\frac{\lambda}{2\lambda+1}\right)^{1/2} \underset{\sim}{c}\cdot\underset{\sim}{T}_{\lambda\lambda-1\mu}(\hat{r})\left(\frac{\lambda+1}{r} + \frac{d}{dr}\right)F(r)$$

$$+ \left(\frac{\lambda+1}{2\lambda+1}\right)^{1/2} \underset{\sim}{c}\cdot\underset{\sim}{T}_{\lambda\lambda+1\mu}(\hat{r})\left(\frac{\lambda}{r} - \frac{d}{dr}\right) F(r). \tag{3.8}$$

This new form in terms of Fourier transforms could have been anticipated, because the radial operations in eqn (3.8) are uniquely those associated with the spherical Bessel functions.

Eqn (3.8) completes the connection with Rose's formula for the gradient. We now extend the analysis given above to the consideration of an arbitrary term in the Taylor series. Thus, we consider the transformation of an arbitrary term from an integral to a differential form in the radial component only.

For a given function $G(\underset{\sim}{r})$, λ is specified. For a given value of the order n, the values of ℓ also are specified. The Clebsch-Gordan coefficients fix the parity and range of the L-values. Thus, it is possible to see that

$$L = \lambda \pm q \tag{3.9}$$

with the values of q fixed and limited by the conditions mentioned. The summation over L in the expression for an arbitrary term in the Taylor series is rewritten as

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = (4\pi)^{3/2}\frac{c^n}{n!}\sum_{\ell,m}(-i)^{n+\lambda}\frac{A_{n\ell}}{[(2\ell+1)(2\ell+1)]^{1/2}}Y_{\ell m}(\hat{c})$$

$$\times\sum_{q=0}^{\ell}\sum_{M}\Bigg[(-i)^q\sqrt{2(\lambda+q)+1}\,(\lambda+q\ell 00|\lambda 0)(\lambda+q\ell Mm|\lambda\mu)Y_{\lambda+qM}(\hat{r})I_{n,\lambda+q}(r)$$

$$+\,(-i)^{-q}\sqrt{2(\lambda-q)+1}\,(\lambda-q\ell 00|\lambda 0)(\lambda-q\ell Mm|\lambda\mu)Y_{\lambda-qM}(\hat{r})I_{n,\lambda-q}(r)\Bigg]. \tag{3.10}$$

In fact, the summations run over $q=0,2,4,6...$ or $q=1,3,5,...$ depending upon the values of n and λ. The factor $A_{n\ell}$ together with the Clebsch-Gordan coefficient automatically sort out the terms which survive in the summation. Hence, there is no need to display any specific form of the sorting process.

We now use the following lowering and raising operators

$$j_{\lambda+q}(kr) = (-1)^q\ r^{\lambda+q}\left(\frac{d}{rdr}\right)^q r^{-\lambda}\{k^{-\lambda}j_\lambda(kr)\} \tag{3.11}$$

and

$$j_{\lambda-q}(kr) = r^{q-\lambda-1}\left(\frac{d}{rdr}\right)^q r^{\lambda+1}\{k^{-q}j_\lambda(kr)\} \tag{3.12}$$

to write

$$(2\pi)^3 I_{n,\lambda+q}(r) = (-1)^q r^{\lambda+q}\left(\frac{d}{rdr}\right)^q r^{-\lambda}\int_0^\infty dk\ k^{n-q+2}f(k)j_\lambda(kr) \tag{3.13}$$

and

$$(2\pi)^3 I_{n,\lambda-q}(r) = r^{q-\lambda-1}\left(\frac{d}{rdr}\right)^q r^{\lambda+1}\int_0^\infty dk\ k^{n-q+2}f(k)j_\lambda(kr) \tag{3.14}$$

For a given value of q in $I_{n,\lambda+q}(r)$ we have adjusted the index on the Bessel function to a value of λ. It remains therefore only to lower the magnitude of the exponent of k in the integrand from k^{n-q+2} to k^2. This we do as follows. First, note that from the various conditions on the parities of the indices, n-q will always be even. Thus, we can reduce n-q to a zero value in steps of 2. From the eigenvalue equation which the Bessel function j_λ satisfies, we write

$$x^2 j_\lambda(x) = \left[\lambda(\lambda+1) - \frac{d}{dx}(x^2\frac{d}{dx})\right] j_\lambda(x). \tag{3.15}$$

The right hand side of this equation defines an operator which lowers the exponent on k (x=kr) by 2. The use of this operator (n-q)/2 times yields the desired result:

$$\int_0^\infty dk\ k^{n-q+2} f(k) j_\lambda(kr) = \left[\lambda(\lambda+1) - \frac{d}{dr}(r^2\frac{d}{dr})\right]^{\frac{n-q}{2}} \int_0^\infty dk\ k^2 f(k) j_\lambda(kr)$$

$$= 2\pi^2 i^\lambda \left[\lambda(\lambda+1) - \frac{d}{dr}(r^2\frac{d}{dr})\right]^{\frac{n-q}{2}} r^{q-n} F(r). \tag{3.16}$$

The final expression for the arbitrary term in the Taylor series is

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = \sqrt{4\pi}\,\frac{c^n}{n!}\sum_{\ell,m}(-i)^n \frac{\Lambda_{n\ell}}{[(2\lambda+1(2\ell+1)]^{1/2}} Y_{\ell m}(\hat{c})$$

$$\times \sum_{q=0}^{\ell}\sum_M i^q \left[\sqrt{2(\lambda+q)+1}(\lambda+q\ell 00|\lambda 0)(\lambda+q\ell Mm|\lambda\mu) Y_{\lambda+qM}(\hat{r}) r^{\lambda+q}\left(\frac{d}{rdr}\right)^q r^{-\lambda}\right.$$

$$\left. + \sqrt{2(\lambda-q)+1}(\lambda-q\ell 00|\lambda 0)(\lambda-q\ell Mm|\lambda\mu) Y_{\lambda-qM}(\hat{r}) r^{q-\lambda-1}\left(\frac{d}{rdr}\right)^q r^{\lambda+1}\right]$$

$$\times\left[\lambda(\lambda+1) - \frac{d}{dr}\left(r^2\frac{d}{dr}\right)\right]^{\frac{n-q}{2}} r^{q-n}F(r). \tag{3.17}$$

4. The Expansion of a Function in a Taylor Series about two Centres

For some applications it is useful to consider the function of eqn (2.1) to depend upon two points $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, either of which may be displaced independently. We set

$$\underset{\sim}{r} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2 \tag{4.1}$$

and redefine

$$G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = Y_{\lambda\mu}(\hat{r})F(r). \tag{4.2}$$

This function still possesses a Fourier transform as expressed by eqn (2.2), (2.3) and (3.7). Before we evaluate this function at displaced points, however, we present an alternative Fourier transform which emphasizes the two-centre character.

Into the expression for the Fourier transform

$$G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = (2\pi)^{-3}\int d^3k\; f(k)Y_{\lambda\mu}(\hat{k})\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}_1)\exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}_2) \tag{4.3}$$

we substitute *two* Rayleigh expansions of the form (2.10). The angular integrations over the three spherical harmonic functions yield

$$G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \frac{2}{\pi}\int_0^\infty dkk^2\int_{4\pi} d\Omega_k f(k) Y_{\lambda\mu}(\hat{k}) \sum_{L_1,M_1,L_2,M_2} (-i)^{L_1}(i)^{L_2}$$

$$\times j_{L_1}(kr_1)Y_{L_1M_1}(\hat{r}_1)Y^*_{L_1M_1}(\hat{k})j_{L_2}(kr_2)Y^*_{L_2M_2}(\hat{r}_2)Y_{L_2M_2}(\hat{k})$$

$$= \frac{1}{\pi^{3/2}} \sum_{L_1M_1L_2M_2} i^{L_2-L_1} Y_{L_1M_1}(\hat{r}_1)Y^*_{L_2M_2}(\hat{r}_2)$$

$$\times\left(\frac{(2L_1+1)(2L_2+1)}{2\lambda+1}\right)^{1/2}(L_1L_2 00|\lambda 0)(L_1L_2M_1M_2|\lambda\mu)$$

$$\times\int_0^\infty dk\ k^2 f(k) j_{L_1}(kr_1) j_{L_2}(kr_2). \qquad (4.4)$$

In order for eqn (4.4) to be consistent with eqn (3.7) and (4.2) for arbitrary functions, we require the following double addition formula for spherical harmonic and Bessel functions:

$$Y_{\lambda\mu}(\hat{r})j_\lambda(kr) = (4\pi)^{1/2} \sum_{L_1M_1L_2M_2} i^{\lambda+L_2-L_1}(L_1L_2 00|\lambda 0)(L_1L_2M_1M_2|\lambda\mu)$$

$$\times\left(\frac{(2L_1+1)(2L_2+1)}{2\lambda+1}\right)^{1/2} Y_{L_1M_1}(\hat{r}_1)j_{L_1}(kr_1)Y_{L_2M_2}(\hat{r}_2)j_{L_2}(kr_2). \qquad (4.5)$$

A similar form for real spherical harmonic functions has been derived by Johnson (1973). It is possible to show easily that the right hand side of (4.5) reduces to the form of the left hand side when $\underset{\sim}{r}_2=0$ and $\underset{\sim}{r}=\underset{\sim}{r}_1$. Additionally, when $\lambda=\mu=0$, the right hand side of (4.5) can be shown to reduce to $Y_{00}(\hat{r})j_0(kr)$ with the use of the appropriate Clebsch-Gordan coefficients and the addition theorem for the spherical harmonic functions. Thus, the two-centre expansion is consistent with the more familiar single-centre forms.

We proceed to evaluate the two-centre function at the displaced

points $\underset{\sim}{r}_1+\underset{\sim}{a}$ and $\underset{\sim}{r}_2+\underset{\sim}{b}$. We have as the extended vectorial Taylor series, the expansion

$$G(\underset{\sim}{r}_1+\underset{\sim}{a},\underset{\sim}{r}_2+\underset{\sim}{b}) = \sum_{n=0}^{\infty} \frac{1}{n!}(\underset{\sim}{a}\cdot\underset{\sim}{\nabla}_1 + \underset{\sim}{b}\cdot\underset{\sim}{\nabla}_2)^n G(\underset{\sim}{r}_1,\underset{\sim}{r}_2). \tag{4.6}$$

The general term in this series is to be evaluated with $G(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ expressed by its Fourier transform [eqn (4.3)]. We have

$$\frac{1}{n!}(\underset{\sim}{a}\cdot\underset{\sim}{\nabla}_1 + \underset{\sim}{b}\cdot\underset{\sim}{\nabla}_2)^n G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = (2\pi)^{-3}\int d^3k\ f(k)Y_{\lambda\mu}(\hat{k})$$

$$\times \frac{1}{n!}[-i\underset{\sim}{a}\cdot\underset{\sim}{k} + i\underset{\sim}{b}\cdot\underset{\sim}{k}]^n \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}_1)\exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}_2). \tag{4.7}$$

In this expression we use the binomial expansion and the expansion in irreducible forms (2.11) to replace the quantity in the brackets:

$$[\underset{\sim}{a}\cdot\underset{\sim}{k} - \underset{\sim}{b}\cdot\underset{\sim}{k}]^n = \sum_q \binom{n}{q}(\underset{\sim}{a}\cdot\underset{\sim}{k})^{n-q}(-\underset{\sim}{b}\cdot\underset{\sim}{k})^q$$

$$= \sum_{q,\ell_1,\ell_2 m_1,m_2} \binom{n}{q} k^n a^{n-q}(-b)^q \frac{(4\pi)^2}{(2\ell_1+1)(2\ell_2+1)}$$

$$\times A_{n-q,\ell_1} A_{q,\ell_2} Y_{\ell_1 m_1}(\hat{a}) Y^*_{\ell_1 m_1}(\hat{k}) Y_{\ell_2 m_2}(\hat{b}) Y^*_{\ell_2 m_2}(\hat{k}). \tag{4.8}$$

The coupling rule for the spherical harmonic functions is now used to reduce the number of these functions in the product (Rose, 1957):

$$Y^*_{\ell_1 m_1}(\hat{k}) Y^*_{\ell_2 m_2}(\hat{k}) = \sum_{\ell,m}\left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell+1)}\right]^{1/2} (\ell_1\ell_2 00|\ell 0)$$

$$\times(\ell_1\ell_2 m_1 m_2|\ell m) Y^*_{\ell m}(\hat{k}). \tag{4.9}$$

The substitution of two Rayleigh expansions, and the use again of the coupling rule together with eqn (4.8) and (4.9) leads to

$$\frac{1}{n!}[\underset{\sim}{a}\cdot\underset{\sim}{\nabla}_1 + \underset{\sim}{b}\cdot\underset{\sim}{\nabla}_2]^n G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \frac{8}{n!}\sum_{q,\ell_1,\ell_2,m_1,m_2,L_1,L_2,M_1,M_2,L,M}$$

$$\times(-i)^{n+L_1-L_2}\binom{n}{q}a^{n-q}(-b)^q A_{n-q,\ell_1}A_{q,\ell_2}Y_{\ell_1m_1}(\hat{a})Y_{\ell_2m_2}(\hat{b})Y_{L_1M_1}(\hat{r}_1)$$

$$\times Y_{L_2M_2}(\hat{r}_2)\left[\frac{(2L_1+1)(2L_2+1)}{(2\ell_1+1)(2\ell_2+1)(2\ell+1)(2L+1)}\right]^{1/2}(\ell_1\ell_2 00|\ell 0)(\ell_1\ell_2 m_1 m_2|\ell m)$$

$$\times(L_1L_2 00|L0)\ (L_1L_2M_1M_2|LM)\int_0^\infty dk\ k^{n+2}j_{L_1}(kr_1)j_{L_2}(kr_2)$$

$$\times\int_{4\pi}d\Omega_k Y_{\lambda\mu}(\hat{k})Y^*_{LM}(\hat{k})Y^*_{\ell m}(\hat{k}). \tag{4.10}$$

The angular integral is evaluated as before (cf., eqn (2.13)), and we introduce another quantity defined by the remaining radial integral:

$$J_{nL_1L_2}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \frac{1}{(2\pi)^3}\int_0^\infty dk\ k^{n+2}f(k)j_{L_1}(kr_1)j_{L_2}(kr_2). \tag{4.11}$$

Thus, we obtain the following expression for the general term in the Taylor expansion of a two-centre function:

$$\frac{1}{n!}[\underset{\sim}{a}\cdot\underset{\sim}{\nabla}_1 + \underset{\sim}{b}\cdot\underset{\sim}{\nabla}_2]^n G(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \frac{4(4\pi)^{3/2}}{n!}\sum_{q,\ell_1,\ell_2,m_1,m_2,L_1,L_2,M_1,M_2,L,M}$$

$$\times(-i)^{n+L_1-L_2}\binom{n}{q}a^{n-q}(-b)^q A_{n-q,\ell_1}A_{q,\ell_2}Y_{\ell_1m_1}(\hat{a})Y_{\ell_2m_2}(\hat{b})Y_{L_1M_1}(\hat{r}_1)$$

$$\times Y_{L_2M_2}(\hat{r}_2)\left[\frac{(2L_1+1)(2L_2+1)}{(2\ell_1+1)(2\ell_2+1)(2\lambda+1)}\right]^{1/2}(\ell_1\ell_2 00|\ell 0)\ (L_1L_2 00|L0)$$

$$\times(\ell L 00|\lambda 0)(\ell_1\ell_2 m_1m_2|\ell m)(L_1L_2M_1M_2|LM)(\ell LmM|\lambda\mu)J_{nL_1L_2}(r_1,r_2). \tag{4.12}$$

Alternate expressions for the expansion about two centres are possible. We present the formula for the general term of the Taylor series for one such modification. In particular, when the vectorial difference $\underset{\sim}{r}_1 - \underset{\sim}{r}_2 = \underset{\sim}{R}$, a vector drawn between two points of reference, is a constant quantity, then the expansion can be considered in terms of displacements about the two ends of the vector $\underset{\sim}{R}$. The formula for the general term is

$$\frac{1}{n!}[\underset{\sim}{a}\cdot\underset{\sim}{\nabla}_1 + \underset{\sim}{b}\cdot\underset{\sim}{\nabla}_2]^n G(\underset{\sim}{R}) = \frac{(4\pi)^2}{n!}\sum_{q,\ell_1,\ell_2,m_1,m_2,\ell,L,M}(-i)^{n+L}$$

$$\times\binom{n}{q}a^{n-q}(-b)^q A_{n-q,\ell_1}A_{q,\ell_2}\left(\frac{2L+1}{(2\ell_1+1)(2\ell_2+1)(2\lambda+1)}\right)^{1/2}$$

$$\times(\ell_1\ell_2 00|\ell 0)(\ell L00|\lambda 0)(\ell_1\ell_2 m_1 m_2|\ell m)(\ell L m M|\lambda\mu)Y_{\ell_1 m_1}(\hat{a})Y_{\ell_2 m_2}(\hat{b})$$

$$\times Y_{LM}(\hat{R})I_{nL}(R) \tag{4.13}$$

in which $I_{nL}(R)$ is defined by eqn (2.14). The analysis which leads to eqn (4.13) parallels the preceeding analyses.

5. Discussion

Many specific examples of functions which can be expanded usefully in Taylor series easily spring to mind. Several examples which can be derived from the Yukawa potential are considered in a companion paper (McKinley and Schmidt, 198_a).

We conclude this paper by showing the limiting forms for the Taylor series when the function to be expanded is scalar.

The scalar function $G(r)$ is expressed as

$$G(\underset{\sim}{r}) = Y_{00}(\hat{r})[\sqrt{4\pi}F(r)]$$
$$= F(r). \qquad (5.1)$$

The Fourier transform of this function is $Y_{00}(\hat{k})f(k)$ with $f(k)$ given by

$$f(k) = (4\pi)^{3/2}\int_0^\infty dr\ r^2F(r)j_0(kr). \qquad (5.2)$$

In terms of this form of scalâr function, the general term for the Taylor series is

$$\frac{1}{n!}\ (\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{r}) = (4\pi)^{3/2}(c^n/n!)\sum_{\ell,m,L,M}(-i)^{n+L}A_{n\ell}Y_{\ell m}(\hat{c})Y_{LM}(\hat{r})$$

$$\times\sqrt{(2L+1)(2\ell+1)}(L\ell 00|00)(L\ell Mm|00)I_{nL}(r)$$

$$= (4\pi)^{3/2}(c^n/n!)\sum_{\ell,m}(-i)^{n+\ell}A_{n\ell}\frac{(-1)^n Y_{\ell -m}(\hat{r})Y_{\ell m}(\hat{c})}{2\ell+1}\ I_{n\ell}(r)$$

$$= \sqrt{4\pi}(c^n/n!)\sum_{\ell}(-i)^{n+\ell}A_{n\ell}P_{\ell}(\hat{r}\cdot\hat{c})I_{n\ell}(r). \qquad (5.3)$$

This quantity is evidently a generalization of the expansion of the Coulomb potential in a Legendre polnomial series:

$$|\underset{\sim}{r}+\underset{\sim}{c}|^{-1} = \sum\frac{(-c)}{r^{\ell+1}}\ P_{\ell}(\hat{r}\cdot\hat{c}). \qquad (5.4)$$

The general differential form also assumes a simpler appearance in the scalar limit. We need only consider the $I_{n\ell}(r)$ quantity in

eqn (5.3). From the definition of $I_{n\ell}(r)$ we have

$$(2\pi)^3 I_{n\ell}(r) = \int_0^\infty dk\ k^{n+2} f(k) j_\ell(kr)$$

$$= 4\pi^{5/2}(-1)^{(n+\ell)/2} r^\ell \left(\frac{d}{rdr}\right)^\ell \frac{1}{r}(d/dr)^{n-\ell} rF(r). \qquad (5.5)$$

Following Todd, Kay and Silverstone (1970), we can show that

$$r^\ell \left(\frac{d}{rdr}\right)^\ell r^{-1}(d/dr)^{n-\ell} rF(r) = \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!} r^{-q}\left(\frac{n-q}{r} + \frac{d}{dr}\right)$$

$$\times (d/dr)^{n-q-1} F(r). \qquad (5.6)$$

Thus,

$$I_{n\ell}(r) = \frac{1}{\sqrt{4\pi}} (-1)^{(n+\ell)/2} \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!} r^{-q}\left(\frac{n-q}{r} + \frac{d}{dr}\right)$$

$$\times (d/dr)^{n-q-1} F(r). \qquad (5.7)$$

For example, the second order term in the Taylor series assumes a simple form: viz.,

$$\frac{1}{2}c^2 \sum_\ell A_{n\ell} P_\ell(\hat{r}\cdot\hat{c}) I_{2\ell}(r) = \frac{1}{2}c^2 \left[\frac{1}{3}\left(\frac{2}{r}\frac{dF}{dr} + \frac{d^2F}{dr^2}\right) - \frac{2}{3}P_2(\hat{r}\cdot\hat{c})\left(\frac{1}{r}\frac{dF}{dr}\right.\right.$$

$$\left.\left. - \frac{d^2F}{dr^2}\right)\right] \qquad (5.8)$$

This form is particularly useful for a number of applications which involve scalar functions.

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References

Band W, 1959, Introduction to Mathematical Physics (New York: van Nostrand)

Briels W J, 1980, J. Chem. Phys., 73, 1850-61

Carlson B C and Rushbrooke G S, 1950, Proc. Camb. Phil. Soc., 46, 626-635

Fano U and Racah G, 1959, Irreducible Tensorial Sets (New York: Academic Press)

Infeld L and Hull T E, 1951, Rev. Mod. Phys., 23, 21-68

Jackson J D, 1962, Classical Electrodynamics (New York: John Wiley & Sons)

McKinley J M and Schmidt P P, 198_a, J. Phys. A (Math. Phys.), 'Taylor-Laplace expansions of the Yukawa and related potential energy functions,' submitted; 198_b, J. Chem. Soc. Faraday II, 'Vibrational and stability analyses for ions and atoms associated with rings and crypts,' submitted

Morse P M and Feshback H, 1953, Methods of Theoretical Physics (New York: McGraw-Hill)

Rose M E, 1957, Elementary Theory of Angular Momentum (New York: John Wiley & Sons)

Schmidt P P, Pons B S & McKinely J M, 1980, JCS Faraday II, 76,979-1007

Todd H D, Kay K G & Silverstone H J, J. Chem. Phys., 53, 3951-56

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